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GB 1379514
GB 1367638
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GB 729871
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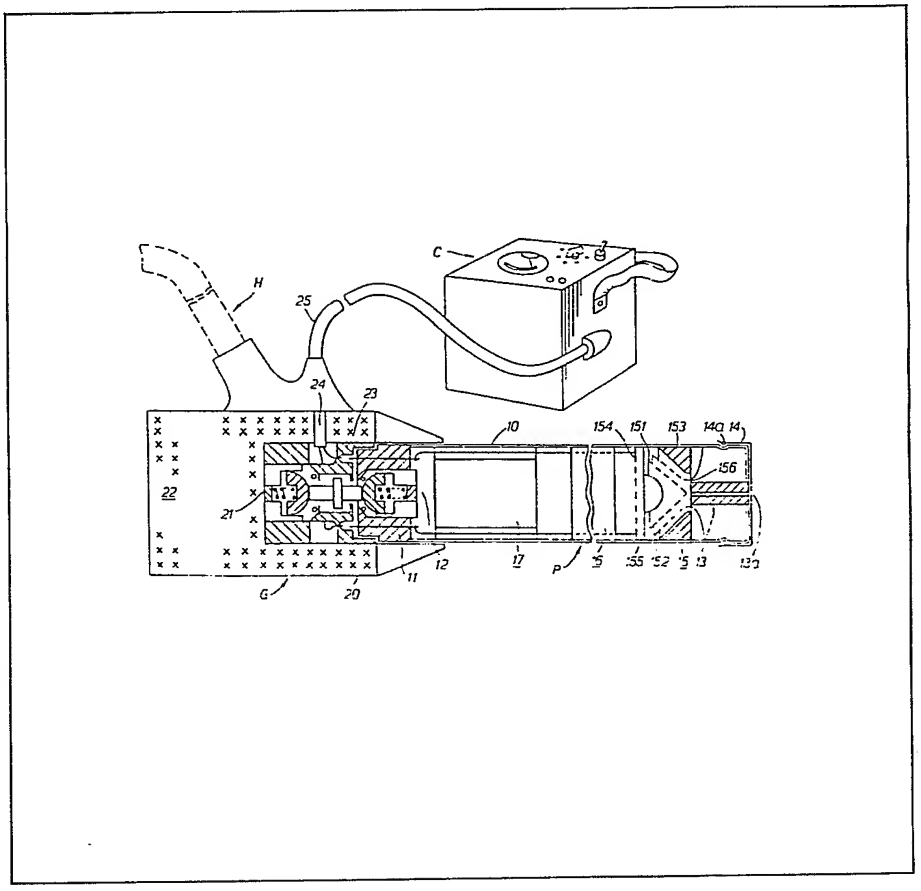
(54) **Mass spectrometers**

(57) A portable mass spectrometer comprises a power pack C and a hand held probe P, the probe comprising a gas inlet 13 with a porous membrane 14, an ion source 15 which can also function as an ion pump, a quadrupole ion filter 16, an ion detector 17 and a chemical getter G to provide a vacuum within the probe. The spectrometer is intended for detecting chemicals in remote areas and does not require a conventional vacuum system. Valves 12 and 21 are provided on the probe P and getter G respectively, both valves being opened when these two parts are engaged.



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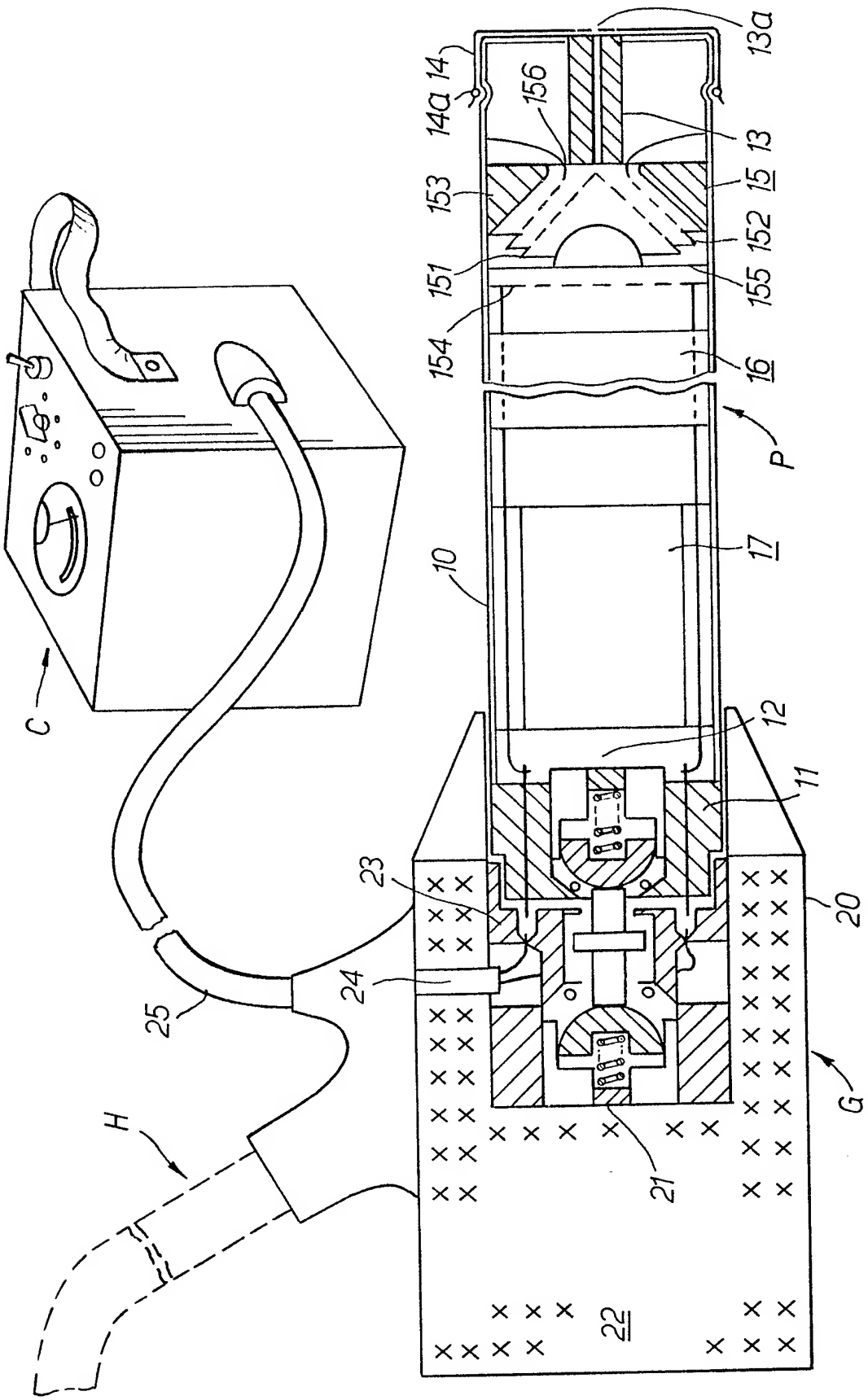
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SPECIFICATION

Improvements in or relating to mass spectrometers

This invention relates to mass spectrometers.

A mass spectrometer generally includes an ion source an ion filter and an ion detector. In operation of the spectrometer the gas pressure around these elements is reduced to a very low level so as to not obstruct the motion of ions. A sample of a gas of interest is introduced, at low pressure, into the ion source which ionizes the gas of interest. The ions thus formed are caused to move towards an ion filter which is operated so as only to allow ions of a selected e/m ratio to pass through it. Ions passing through the ion filter reach an ion detector which provides an output signal indicating that ions have passed through filter. The output signal provides an indication of the ions obtainable from the gas of interest and this indication can be interpreted to provide information as to the nature of the gas of interest.

A mass spectrometer of the general type referred to above is described in U.K. Patent Specification 1379514 and 1379515. Mass spectrometers of this and other types as proposed hitherto require an external vacuum pump to establish and maintain the vacuum necessary around the elements of the spectrometer for satisfactory operation of the device.

It is an object of the present invention to provide a mass spectrometer which is compact and does not require the provision of an external vacuum apparatus for its operation.

According to the invention there is provided a mass spectrometer arrangement comprising a probe member which includes an evacuable housing having a gas inlet, an ion control means capable of ionising gas received through the inlet, an ion filter means disposed adjacent to the control means to receive ions produced thereby, adjacent to the output from the filter means an ion detection means capable of producing an output signal indicative of ions passing through the filter and a power supply for the control, filter and detection means, the arrangement also comprising a container for a chemical getter material, the probe and container being separable and each having a valve means which cooperate to couple the container and the probe housing to permit the getter material to evacuate the housing.

Each valve means may comprise a valve element which is resiliently biassed to seal respective apertures in the probe housing and the container, which elements are arranged to be held away from the aperture, against the resilient bias, when the probe and container are coupled. Each valve element may be a hemispherical member which engages a rubber "0" ring surrounding the said aperture to create the seal.

The ion control means may comprise a pair of nested frusto conical members, the inner member being of a mesh form, means for setting the outer member at a d.c. potential relative to the inner member and also means for applying an r.f. potential between the members.

The ion control means may be selectively operable as an ion source and an ion pump, the control means comprising a pair of nested frusto conical members, both of a mesh form, an annulus of a getter material disposed adjacent to the outer member and means for applying r.f. and d.c. potentials between the members, so that when the control means is used as an ion source the outer member is held at a first d.c. potential relative to the inner member, and when the control means is used as an ion pump the outer member is held at a sufficiently large d.c. potential relative to the inner member and to the annulus of getter material, and of an opposite polarity to the first d.c. potential to cause the ions to impinge substantially on the getter material.

According to another aspect of the invention there is also provided a probe member for use in a mass spectrometer as described above.

Embodiments of the invention will now be described with reference to the accompanying drawing which shows a mass spectrometer embodying the invention.

Referring to the drawing the mass spectrometer has three main parts, a probe P, a getter body G and a control unit C. The probe is a cylindrical object from 0.5 to 0.75 inch (12 - 18mm) diameter and from 10 inch (250mm) in length. The probe plugs into a getter body which is of a size to be comfortably held in the hand and to contain a quantity of chemical getter to be described below. The probe makes electrical and mechanical connections to the getter body when it is plugged in place. The multi-core electrical connector extends from the getter body to the control unit C. The control unit contains an electrical power source such as primary or rechargeable batteries together with controls and display means by which the mass spectrometer may be operated to detect gases of interest. As an alternative to hand-held operation an extension handle H may be fitted to the getter body to ease use at ground level by a walking operator or to reach otherwise inaccessible points.

The probe P has a cylindrical body 10 of an electrically-insulating material which is also suitable for enclosing an evacuated space. One suitable material for the envelope is a tube of glass with an outer metal tube to provide mechanical protection. The tube 10 is closed at one end by a multi-pin plug 11 in the middle of which is a gas control valve 12. The other end of the tube 10 has a gas inlet 13 in the form of a length of capillary tube seal thereto to provide a restricted gas inlet to within the envelope. The outermost end of tube 13 has a micro mesh grid 13a to support a porous membrane 14 across the bore of the tube 13. The membrane 14 may be held in place by a resilient ring 14a around the body of the probe. The ring 14a may be sized to make a gas-type fit between the probe and the getter body G when the probe is reversed and inserted into the getter body. The getter body may be a sealed unit replaceable with another without dismantling the equipment, being slid onto the handle H around the base 23.

The following ion-handling elements are arranged

in sequence between the inlet 13 and the base 11 within the probe body. An ion control stage 15 is next to the inlet 13 and is followed by an ion filter 16. Ions passed through the ion filter 16 are detected by an ion detector 17 which then supplies an appropriate electrical output signal to a conductor connected to one of the pins in the base 11. Suitable electrical connections are provided from the pins of base 11 to the ion handling elements spaced along the probe body. Considering the elements in more detail in turn the ion control stage 15 is selectively operable as an ion source and an ion pump. In a preferred embodiment ion control stage 15 is constructed onto two nested frusto-conical members 151, 152 as electrodes of a conductive mesh material. An annular body 153, of an ion getter material such as titanium, surrounds the outer conical member 152. In operation of the ion control stage 15 ions from gas which enters the probe along the tube 13 are selectively directed to the getter 153 or to electrodes 154, 155 in dependence on the potentials applied to electrodes 151 and 152. Electrodes 154 and 155 respectively form the focussing electrode and an extractor electrode and cause ions to be directed into the ion filter 16.

Ion filter 16 is preferably a body of ceramic having a bore defined by one or more hyperbolic surfaces each having a conductive coating to form individual electrodes. One form of such an ion filter is described in U.K. Patent Specification 1367638. While the filter described in U.K. Patent Specification 1367638 provides excellent filter characteristics for laboratory and similar large-scale instruments its size and power requirements make it less suitable for portable instruments and preferably the ion filter is of a more compact form. Such a compact ion filter which is particularly suitable for use with ions of mass ratio up to 200 is of quadrupole form and comprises a cylidrincal ceramic body having an axial passage of a cross-section formed by the intersection with a circle of four equal symmetricly disposed convex rectangular hyperbolic sections, the ratio of the diameter of said circle to the minimum cross-sectional dimension of the passage being from 1.4 to 1.8 provided that said minimum cross-sectional dimension is sufficiently large so that in operation a field is maintained such that transmission of ions is preserved. The hyperbolic surfaces of the passage have a conductive coating and form the quadrupoles of the ion filter, being electrically isolated from each other by the circular surfaces which are insulated.

In such a construction the latus rectum of each hyperbolic surface is substantially completely included within said circle and theoretical calculations have shown that this is a necessary condition for maintaining reasonably efficient operation. Such a filter can be constructed having an outside diameter of less than 0.5".

Ions which pass through the filter 16 are detected by electron multiplier 17 which may be of conventional form as used in mass spectrometers. A probe as described so far can be constructed in a tube of approximately 0.5 inch (12mm) diameter and makes use of a standard range of electron multipliers which fit a tube of such a diameter. A filter of the type described for example, in UK Patent Specification No. 1367638 may alternatively be used.

The chemical getter in container G is a material such as aluminium-zirconium which is capable of absorbing gas and is provided in sufficient quantity to exhaust the space inside the probe P to a pressure of not more than 1 torr. As the capacity of getter to exhaust the probe is limited, valves are provided on base 21 in the getter container and at 12 on the probe base to seal the respective volumes against the atmosphere. Preferably the valves 12 and 21 are generally of similar form having a hemispherical valve element spring-urged to seal and reseal the entrance of the container or probe by contact with an 0-ring around the entrance. The hemispherical elements are preferably guided by ribs in the bore to permit the passage of gas through the bore with extension on the ribs also guiding the spring. One of the valves, preferably that in the getter container G, is provided with a follower to ensure that both valves are lifted off their seats when the probe and getter container are engaged with one another as shown in the drawing. The getter container G is formed by a case 20 enclosing a quantity of the getter material, 22, and the valve 21. Electrical socket 23, for example of the valve-base type, suitable to receive the plug 11 on probe P is also provided and a multi-way electrical conductor 25 extends from the socket 23 and out of the container. The valves permit the separation and reconnection or exchange of probes and getter bodies.

The probe of the present invention could be used in connection with any source for evacuating the interior of the probe to a level such as 1 torr, for example, as described above. Such sources are relatively cheap and easily available and for a portable apparatus the chemical getter means described above is preferred. However, it is an important feature of our invention that by switching the probe to the ion pump mode such an easily attainable level of vacuum (which we will hereinafter refer to as a "rough" vacuum) can be reduced to the much lower pressures which are required for the operation of mass spectrometry.

Control unit C may be carried hung around an operator's neck to rest on his chest.

Connector 25 extends to the control unit C and provides connections as mentioned above. Connector 25 may be arranged to extend along the axis of the unit and emerge through the end of portion G rather than radially as shown.

The operation of the arrangement is as follows:- The probe P is produced as a unit and during its manufacture the membrane 14 is constructed to be suitable for the gas or gases which are of interest for the instrument. If required the porosity of the membrane 14 can be adjusted during manufacture by spraying material, such as silicone rubber, onto it in known manner. Gas-selective material for membrane 14 such as silicone rubber and cellulose are well known. Other membranes and membrane forms may be used as appropriate. To bring the arrangement into action the probe is plugged into the getter container as shown in the drawing and the control unit switched on. The chemical getter mate-

rial 22 exhausts the inside of the probe down to a pressure of no greater than 1 torr and gas of interest will begin to transfer through the membrane 14 into the inside of the probe. The ion control stage 15 is then operated as an ion pump to reduce the pressure to below 10^{-4} and preferably to no more than 2×10^{-6} torr. To operate as an ion pump the electrodes 151, 152 are energised with both a d.c. potential and an alternating potential at a high frequency. The exact frequency will depend on the nature of the gases of interest but is typically in the order of 1 to 4 KHz. For a probe of a tube of approximately ½ inch diameter the d.c. potential is approximately 800 volts with electrode 151 being at earth potential and electrode 152 having a negative polarity, while the alternating potential has an amplitude of some 2.5kv peak-to-peak. The getter body 153 is also at earth potential and the arrangement is such that the d.c. bias in combination with the alernating potential ensures that all ions are accelerated into the getter 153. In this way the pressure in the probe is reduced to the required level. When this low required level. When this low pressure has been achieved the potentials of electrodes 151 and 152 are altered to provide operation as an ion source. Electrode 152 is now supplied with a d.c. potential to make it some 170 volts positive with respect to the earth electrode 151 while the alternating potential is maintained. During the negative-going half cycles of the alternating potential ions are still swept to the getter 153, however during the positive-going half cycle ions are focussed onto the centre of curvature of electrode 155 and slowed down by the combined action of electrode 155 and 154 to have an energy of some 5 - 8 e.v. to control entry to the ion filter 16. The ion filter 16 is energised with a high-frequency alternating potential to permit only those ions with an appropriate e/m ratio to pass through the filter to the ion detector 17. The conditions to achieve such filtering are well known in the art. The same high frequency potential may be used both for the ion control stage 15 and for the ion filter stage 16. The power of some 15 watts of high frequency potential is required for a probe of the size described above. The high frequency potential may be generated with the inlet control unit C or in the probe itself. The generator of the high frequency must be positioned with care and regard to various factors. If the generator is in unit C there will be losses in the supply leads but less interference, if the generator is in the probe this will be larger and heavier and there may be interference by radiation within the probe. In selecting the high frequency for the ion control stage 15 consideration must be given to the time taken for ions to reach the getter body 153 as, if the potential was reversed before ions had reached the getter they will not be collected by the getter and removed. The 1 to 4 KHz frequency is preferably modulated at a lower frequency, say less than 2KHz, to allow time for the proper sweeping of the ion pump. Too high a frequency allows space charge to accumulate from ions which cannot travel to an electrode before a field reversal occurs. A frequency of some 300 to 500 KHz is generally suitable for one form of operation to ensure removal of these ions.

Signals from the detector 17 can be assessed in the control unit in the usual manner and the presence of gases of interest can be indicated on a meter in the control unit. Other suitable displays clearly may be used instead. The d.c. potentials referred to above are suitable where the ions of interest are positive. For negative ions of interest the d.c. potentials may be reversed. This is particularly important for those materials, e.g. isomers, whose positive ion spectra are similar but whose negative spectra are distinct.

The mass spectrometer arrangement described above provides a self-contained, compact and portable device capable of several hours of operation from a power supply contained within it.

The above arrangement is therefore most useful in areas and conditions where mains electrical supply is not available for example when searching an area for lost, hidden or spilled chemicals which may be dangerous.

CLAIMS

1. A mass spectrometer arrangement comprising a probe member which includes an evacuable housing having a gas inlet, an ion control means capable of ionising gas received through the inlet, an ion filter means disposed adjacent to the control means to receive ions produced thereby, adjacent to the output from the filter means an ion detection means capable of producing an output signal indicative of ions passing through the filter and a power supply for the control, filter and detection means, the arrangement also comprising a container for a chemical getter material, the probe and container being separable and each having a valve means which cooperate to couple the container and the probe housing to permit the getter material to evacuate the housing.

2. A mass spectrometer arrangement according to Claim 1 wherein each said valve means comprises a valve element which is resiliently biased to seal respective apertures in the proble housing and the container, which elements are arranged to be held away from the apertures, against the resilient bias, when the probe and container are coupled.

3. A mass spectrometer arrangement according to Claim 2 wherein each valve element is a hemispherical member which engages a rubber "0" ring surrounding a respective said aperture to create the seal.

4. A mass spectrometer arrangement according to Claims 1 to 3 wherein the ion control means comprises a pair of nested frusto conical members, the inner member being of a mesh form means for setting the outer member at a d.c. potential relative to the inner member and also for applying an r.f. potential between the members.

5. A mass spectrometer arrangement according to Claims 1 to 4 wherein the ion control means is selectively operable as an ion source and an ion pump, the control means comprising a pair of nested frusto conical members both of a mesh form, an annulus of a getter material disposed adjacent to the outer material and means for applying r.f. and d.c.

potentials between the members, so that when the control means is used as an ion source the outer member is held at a first d.c. potential relative to the inner member, and when the control means is used as an ion pump the outer member is held at a sufficiently large d.c. potential relative to the inner member and to the annulus of getter material, and of an opposite polarity to the first d.c. potential to cause ions to impinge substantially on the getter material.

6. A probe member for use in a mass spectrometer arrangement according to any of the preceding claims.

7. A probe member for use in the mass spectrometer arrangement according to Claim 5 which probe member when connected to an evacuating source providing a rough vacuum, as hereinbefore defined, is capable by operation in the ion pump mode of further reducing the pressure to a level at which mass spectrometry can be carried out.

8. A mass spectrometer arrangement, as hereinbefore described, by reference to and as illustrated in the accompanying drawing.

9. A probe member for use in the mass spectrometer arrangement according to Claim 8.

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